

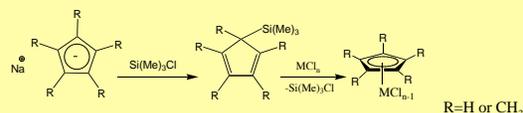
Diversions and Successes on the way to Polyphenylcyclopentadienylniobiumtetrachloride complexes

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INTRODUCTION

This group has been active in the use of pentaaryl cyclopentadienyl ligands in group 4 metal complexes by the application of bulky polyphenyl-cyclopentadienyl groups to exploit their steric bulk as facially directing groups. We have successfully prepared pentaphenylcyclopentadienyl zirconium trichloride ($C_5Ph_5ZrCl_3$) as well as some chiral derivatives,^{1,2} and wish to investigate polyphenylcyclopentadienyl complexes with other metals.

Trimethylsilylcyclopentadienes ($C_5R_5SiMe_3$, R=H, alkyl) have been widely used to transfer a cyclopentadienyl ring to a transition metal. Among the trimethylsilyl (TMS) substituted cyclopentadienes, $C_5Me_5SiMe_3$ has been synthesized to make pentamethylcyclopentadienyl complexes.^{3,4}



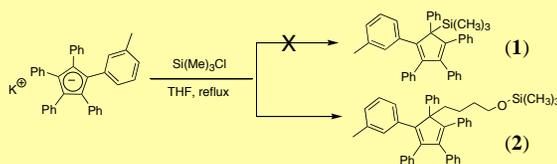
Here we report the synthesis of trimethylsilylpolyphenylcyclopentadienes $C_5(H)Ph_4SiMe_3$, an unexpected product obtained while attempting the pentaphenyl(TMS)cyclopentadienyl, and initial results in polyphenyl-TMS-cyclopentadienyl addition to niobium halides by elimination of $SiMe_3Cl$.

RESULTS and DISCUSSION

1. The Reaction of potassium *m*-tolyltetraphenylcyclopentadienide (*mt*-Cp) with $Si(Me)_3Cl$:

Attempts to prepare trimethylsilyl-*mt*-Cp by the reaction of potassium *mt*-Cp with $Si(Me)_3Cl$ in a variety of solvents (polar, nonpolar organics and neat TMS-Cl) returned only starting material with the exception of tetrahydrofuran (THF). Removal of solvent in vacuo, followed by crystallization in heptane gives an off-white solid. The ¹³C and ¹H NMR spectra as well as HRMS analysis indicate this compound is trimethyl-*m*-tolyltetraphenylcyclopentadienyl-butoxy]-silane(2), the result of THF ring-opening product.

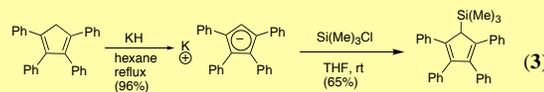
The reaction of potassium *mt*-Cp with $Si(Me)_3Cl$:



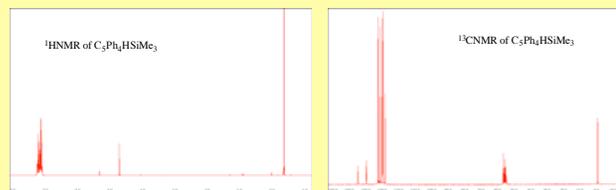
Instead of the formation of the expected product $C_5Ph_5SiMe_3$ (1), the reaction gives a product of THF ring-opened ether (2). The scheme only shows one of three isomers of (2). The reason for this unexpected reaction course may be due to bigger steric hindrance of the five phenyl groups compared to the methyl groups on the pentamethylcyclopentadienyl rings leading to lower reactivity.

2. The Reaction of potassium tetraphenylcyclopentadienide (*KCp*) with $Si(Me)_3Cl$:

Suspecting that a less sterically encumbered polyaryl-cyclopentadiene would be more amenable to addition of the TMS group, reaction using tetraaryl-cyclopentadienide was attempted and trimethylsilyltetraphenylcyclopentadiene $C_5Ph_4HSiMe_3$ (3) was successfully synthesized, and characterized by NMR and HRMS.



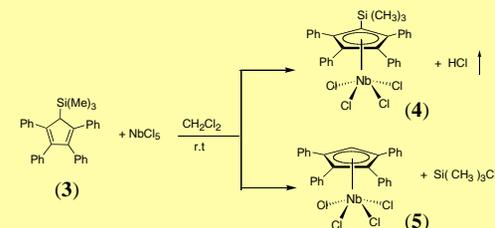
NMR spectra of trimethylsilyltetraphenylcyclopentadiene (3) :



3. The new precursor $C_5Ph_4HSiMe_3$ and its reaction with $NbCl_5$:

Trimethylsilyltetraphenylcyclopentadiene, $C_5Ph_4H-SiMe_3$ was first time synthesized and this adds a new precursor to the trimethylsilyldiene series. Hopefully this new ligand with its steric bulk will provide not only blocking capability, but also discourages dimer and oligomer formation, so the open coordination sites in its complexes are available to bind substrates instead of participating in bridge-bond formation.

The reaction of $C_5Ph_4HSiMe_3$ and $NbCl_5$ was carried out in CH_2Cl_2 as solvent at room temperature. The product of the reaction is a dark red mixture, show as below:



Surprisingly, the reaction does not completely follow the regular route to eliminate the TMS group in $C_5Ph_4HSiMe_3$ to form (5), but shows competitive reactions between elimination of TMS and HCl to form both (4) and (5). Separation and characterization of these two compounds are under process.

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